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(54) Method and apparatus for writing by the emission of atoms

Methode und Gerät zum Schreiben mittels Atomemission

Méthode et appareil pour écriture par émission atomique

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Description

This invention relates to a method and means for depositing atoms on a surface of a substrate.

The basic patent describing a scanning tunnelling microscope (STM) is U.S. patent 4,343,993. An STM is an instrument capable of sensing atomic scale variations in the height of a surface by maintaining tunnelling current constant as the surface is being scanned. This STM technology has been extended to various applications employing a tunnelling tip in close proximity to a surface for producing surface modifications.

U.S. patent 4,829,507 discloses a method of writing indicia on an adsorbent carrier surface of a recording medium by using a tunnelling tip and adding individual atomic particles to the surface from a source other than the tip.

An article in the February 1, 1988 issue of Journal of Applied Physics at pp. 717-721, discloses the use of a tunnelling tip of platinum-iridium material which is moved to within current tunnelling range of a gold surface which is coated with a fluorocarbon grease. Applying a voltage of roughly 1 volt between the tip and surface for roughly 1 second results in a balling up of the gold under the tip, leaving a small well-defined bump. Gold is preferred under ambient conditions because it does not oxidise, and the grease provides an additional protective coating. Platinum-iridium tips are commercially available and inert. This process has the disadvantage of being slow since voltage pulses of approximately 1 second are required.

U.S. patent 4,896,044 discloses use of a tunnelling tip which is moved within current tunnelling range over a gold surface to remove gold atoms from the surface and thereby pit the surface at selected locations for writing indicia thereat.

The unexamined Japanese Patent Application published November 1, 1988 as 63-265101 in the Patent Abstracts of Japan discloses a way to reform a STM tip by applying a high voltage to it, causing atoms to be evaporated in the high electric field. There is no teaching or even suggestion of collecting the emitted atoms for any purpose, nor any reason to believe that such evaporation might be localised and continuous as part of a writing process.

WO-A-88/04470 discloses generation of surface structures of atomic dimensions on substrate surfaces by means of an electron beam, using a raster tunnel microscope to generate a high local current density of tunnel electrons.

Now according to the present invention there is provided a method of writing onto a receiving surface by the emission of atoms from a source of the atoms wherein the source is a scanning probe of wire having a tip positioned within atom transfer range of the receiving surface, the tip is scanned laterally over the receiving surface whilst being subjected to a series of voltage pulses which are of a magnitude and duration to cause

the emission of atoms from the wire onto the receiving surface, and the voltage pulses are effective to cause the tip of the probe to be continually reformed by migration of atoms of the wire probe to the tip.

Further according to the present invention there is provided apparatus for writing onto a receiving surface by the emission of atoms from a source of the atoms, wherein the source is the tip of a scanning wire probe and the apparatus comprises means for holding the tip within atom transfer range of the receiving surface, means to scan the probe tip laterally over the receiving surface and means to apply a series of voltage pulses to the wire to cause the emission of atoms therefrom, the material of the wire being subject to the migration of atoms to reform the tip continually under the influence of the voltage pulses.

This apparatus can be used either for reading or for erasing the writing formed by the method according to the present invention.

Thus submicron structures can be written on a receiving surface by positioning in nanometre range proximity, preferably within the current tunnelling range, of the surface a scanning tip of a wire material that emits atoms upon application of an applied voltage of low magnitude. While the wire tip is maintained within said range, it is moved relative to the surface, and a series of short voltage pulses are concurrently applied between the tip and surface. These pulses cause atoms of tip material to directly transfer to the surface and concurrently cause remaining atoms of tip material to migrate to the tip and continuously reform the tip and maintain its sharp configuration, thereby insuring uninterrupted writing ability. Various tip materials exhibiting low field evaporation potentials may be used; however, gold is preferred if deposition is to be under ambient conditions. Heating the tip enhances the ability of the material to emit atoms. The deposited structures may be selectively sensed or erased by application of appropriate voltages.

Fig. 1 is a simplified schematic diagram of an apparatus according to the invention.

Fig. 1 depicts the basic components of a scanning apparatus required to practice the method according to the invention. As illustrated, the apparatus (like an STM) comprises a conducting wire probe 10 having a sharp scanning tip 11 that preferably is disposed within tunnelling current range (e.g., less than 2nm) of an adsorbent surface 12 on a conductive substrate 13. Probe 10 and hence tip 11 are movable in x, y and z directions relative to surface 12 by piezo drives 14, 15, 16, respectively. Scan control means 17 is connected via drives 14, 15 and 16 to probe 10 to control movement of the probe tip 11 relative to substrate 13. A servo control means 18 is connected to z drive 16 to respond to variations in tunnelling current so as to maintain a constant tip/surface separation. For additional description, if desired, the reader is referred to U.S. patents 4,343,993, 4,575,822 or 4,829,507.

The wire probe 10 is composed of a material that

emits atoms when a voltage of low magnitude is applied to substrate 13 from a suitable source 19. Source 19 may be a Model 8112A voltage pulse generator marketed by the Hewlett-Packard Company.

To write a submicron structure on surface 12, scan control means 17 conditions drive 16 to move in the z direction to bring tip 11 within current tunnelling range from surface 12. Then scan control means 17 conditions drives 14,15 to move probe 10 in the x and/or y directions relative to surface 12 while a series of short voltage pulses are applied between tip 11 and surface 12 to cause atoms of the wire material to transfer directly to said surface and deposit as marks 20 thereon. The typical size of these bumps or marks 20 is of the order of 10nm, which would provide for storage application areal densities greater than 10.18×10^{12} bits/cm sq. As these atoms transfer to surface 12, the electric field applied between tip 11 and surface 12 causes atoms 21 of the wire probe to migrate toward the end of the tip. This continuously reforms tip 11 to maintain its sharp configuration.

Thus, according to an important feature of the invention, tip 11 "heals" itself because as atoms at the tip are pulled off, they are replaced by other atoms 21 of the tip material. This desirably and unexpectedly insures uninterrupted writing ability of the tip. This atom emission phenomenon is not fully understood, but it is believed that the atoms are transferred from the tip to the surface by field evaporation emission, which is enhanced by the close proximity between tip 11 and surface 12.

Tip 11 is preferably of gold because gold does not oxidise and the atom transfer can thus be performed under ambient pressure and temperature conditions. The electric field required for field evaporation from gold is also relatively low, as can be determined from a table of Field Evaporation Data found on pp. 212-213 of an article in Vol. 70 (1978) of Surface Science. Tip 11 must be sharp. Preferably it is electrochemically etched from gold wire; e.g., by immersing the tip portion of the probe in an etchant of concentrated hydrochloric acid and applying about 2v direct current to the etchant. This etching method can provide a tip having a radius of less than one micron. Such a tip is relatively inert and hence very suitable for use as a scanning tip.

In actual test, deposition was performed on a gold (111) surface prepared by melting a gold wire in a torch to obtain a faceted surface (although the surface may, if preferred, be prepared by growing a gold film epitaxially on mica). With gold tip 11 within current tunnelling range of surface 12, virtually 100% probability of atomic particle transfer was achieved when voltage pulses of 4.0V height and a width of 500ns to as little as 100ns were applied between the tip and substrate and when voltage pulses of 5.0V height and widths as little as 10ns were applied between the tip and substrate. In both cases, structures less than 10nm in diameter were deposited. The polarity of the tip 11 with respect to surface 12

can be either positive or negative. However, it has been observed in actual tests that writing is more controllable when tip 11 is negative with respect to surface 12.

It was noted that, after writing over 2000 marks, there was no significant degradation of the tip and writing ability continued unimpaired. Also, when marks (like 20) were written and then examined at much later times, no significant diffusion of the deposited structures was observed. If, over an extended period, diffusion does occur however, it may be effectively eliminated by using a substrate surface to which the material deposited from the tip 11 is strongly bonded.

The method and apparatus were also employed for writing submicron structures on a silicon surface, thus demonstrating the capability to deposit nanometer-size circuit elements. Thus, surface 12 may be on a data storage medium, with the transferred atoms constituting bits of data; or the surface may be part of an electronic circuit, with the transferred atoms collectively constituting circuit elements; or the surface may be part of a mask used to lithographically form integrated circuits.

While tip 11 preferably is of gold, it may if desired be of silver, lead, copper, indium, cobalt, nickel, iron, niobium, titanium, platinum, or aluminium. All of these materials are known to require substantially less electric field for field evaporation than tungsten, which is typically used as the tunnelling tip material. By heating probe 10 and hence tip 11 while write pulses are being applied, the ability of these probe materials to emit atoms can be enhanced or facilitated; this, in turn, may reduce the time and voltage required for atom transfer.

To read the bumps or other submicron structures (like circuit elements or mask elements) thus deposited, scan control means 17 acts through z drive 16 to move probe 10 toward surface 12 to bring tip 11 to within current tunnelling range while a substantially reduced voltage (e.g., about 0.1-1.0V) is maintained by source 19 between the tip and substrate. Tunnelling current between tip and substrate is then sensed by a read amplifier 22. As tip 11 scans surface 12, changes in topography caused by the written marks 20 will modulate the tip/surface separation distances. This in turn will cause substantial modulation in the tunnel current at the amplifier 22. The amplified signal is fed to servo control means 18 as an electronic servo feedback to cause z drive 16 to maintain the tip/surface separation constant. As illustrated, a sensor 23 senses and records variations in the output of the current amplifier 22; however, if preferred, the readout signal may be the output signal generated by servo control means 18 to the z drive 16 in response to this amplifier output.

Erasing can be achieved by selectively removing the atoms which form the marks 20. This can be done by positioning tip 11 directly over a selected mark and applying an erase pulse of appropriate voltage between the tip and surface. Instead of depositing additional atoms on surface 12, atoms are removed from the surface. This is because the selected mark 20, which is it-

self a very sharp feature, now becomes the "tip", and emits atoms upon application of the voltage pulse because the transfer will occur from the tip 11 or the mark 20 depending upon which is sharper.

It should also be noted that while tip/surface separation for writing and reading the marks 20 (or circuit or mask elements) has been described hereinabove as being maintained with a scanning apparatus that senses changes in tunnelling current, any technique which is sensitive to variations in tip/surface separation, such as measuring capacitance or atomic forces, can be employed provided it has the necessary resolution.

As thus far described, the method has been practised by positioning and then moving tip 11 within current tunnelling range of surface 12. This is preferred to reduce the magnitude of the voltage required between tip 11 and substrate 13 to effect atomic particle transfer as both the voltage and mark size increase with tip/surface separation. However, applicants have found that transfer can be effected even if tip 11 is positioned beyond the current tunnelling range (such as at 2nm from surface 12) provided higher voltage pulses are applied between the tip and surface. Hence, the term "atom transfer range" is intended generically to denote a tip/surface separation range at which transfer can occur, whether within or beyond the current tunnelling range. Applicants found that the voltage required between tip 11 and surface 12 to effect deposition should be at least 2V/nm separation distance.

In summary, atoms of and from a sharp tip of a scanning apparatus are directly transferred by short, low voltage pulses to a surface by a "self-healing" technique by which atoms migrate to the tip to continuously replenish those transferred. Submicron structures, in the form of circuit elements or mask elements or data bits, less than 10nm in diameter are created on the surface in as little as 10ns without requiring a developing step or use of a liquid on the surface. Transfer may be effected in air under ambient temperature and pressure conditions.

Claims

1. A method of writing onto a receiving surface by the emission of atoms from a source of the atoms wherein the source is a scanning probe of wire having a tip positioned within atom transfer range of the receiving surface, characterised in that the tip is scanned laterally over the receiving surface whilst being subjected to a series of voltage pulses which are of a magnitude and duration to cause the emission of atoms from the wire onto the receiving surface, and the voltage pulses are effective to cause the tip of the probe to be continually reformed by migration of atoms of the wire probe to the tip.
2. A method according to claim 1 wherein the tip is positioned within current tunnelling range of the re-

ceiving surface.

3. A method according to claim 2 further comprising the step of sensing variations in tunnelling current between the tip and the receiving surface to control the positioning of the tip.
4. A method according to claim 1, 2 or 3 wherein the wire is made of a material selected from gold, silver, lead, copper, indium, cobalt, nickel, iron, niobium, platinum, titanium or aluminium.
5. A method according to any one of the preceding claims wherein the wire is heated.
6. A method according to any one of the claims 1 to 4 wherein the wire is of gold and is unheated.
7. A method according to any one of the preceding claims wherein the voltage applied to the wire exceeds 2 volts per nanometer of distance separating the tip from the receiving surface.
8. A method according to any one of the preceding claims wherein the voltage applied to the wire has a negative polarity relative to the receiving surface.
9. Apparatus for writing onto a receiving surface by the emission of atoms from a source of the atoms, wherein the source is the tip of a scanning wire probe and the apparatus includes means for holding the tip within atom transfer range of the receiving surface, characterised in that the apparatus also includes means to scan the probe tip laterally over the receiving surface and means to apply a series of voltage pulses to the wire to cause the emission of atoms therefrom, the material of the wire being subject to the migration of atoms to reform the tip continually under the influence of the voltage pulses.
10. Use of an apparatus according to claim 9 for reading the writing formed by the method of any of the claims 1 to 8 comprising the steps of scanning the said tip over the writing on the receiving surface and sensing variation in a tunnelling current between the tip and the receiving surface.
11. Use of an apparatus according to claim 9 for erasing the writing formed by the method of any one of claims 1 to 8 wherein said tip is positioned within current tunnelling range of the deposited atoms and the tip is subjected to voltage pulses of a magnitude and polarity to attract the deposited atoms onto the tip.

Patentsprüche

1. Verfahren zum Schreiben auf eine Empfangsfläche mittels der Emission von Atomen aus einer Quelle der Atome, wobei die Quelle ein abrasternder Fühler aus Draht mit einer Spitze ist, die innerhalb des Atomtransferbereichs der Empfangsfläche positioniert ist, dadurch gekennzeichnet, daß die Spitze lateral abrasternd über die Empfangsfläche hinweg geführt wird, während sie einer Reihe von Spannungsimpulsen unterworfen wird, die eine solche Höhe und Dauer aufweisen, daß die Emission von Atomen aus dem Draht auf die Empfangsfläche bewirkt wird, und dadurch, daß die Spannungsimpulse bewirken, daß die Spitze des Fühlers veranlaßt wird, sich durch Migration von Atomen des Fühlers aus Draht zu der Spitze hin kontinuierlich neu zu bilden. 5
2. Verfahren gemäß Anspruch 1, wobei die Spitze innerhalb des Tunnelstrombereichs der Empfangsfläche positioniert wird. 10
3. Verfahren gemäß Anspruch 2, das des weiteren den Schritt der Erfassung von Schwankungen des Tunnelstroms zwischen der Spitze und der Empfangsfläche beinhaltet, um die Positionierung der Spitze zu steuern. 15
4. Verfahren gemäß Anspruch 1, 2 oder 3, wobei der Draht aus einem Material besteht, das aus Gold, Silber, Blei, Kupfer, Indium, Kobalt, Nickel, Eisen, Niob, Platin, Titan oder Aluminium ausgewählt wird. 20
5. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, wobei der Draht erwärmt wird. 25
6. Verfahren gemäß irgendeinem der Ansprüche 1 bis 4, wobei der Draht aus Gold besteht und nicht erwärmt wird. 30
7. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, wobei die an den Draht angelegte Spannung 2 Volt pro Nanometer Abstand, der die Spitze von der Empfangsfläche trennt, übersteigt. 35
8. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, wobei die an den Draht angelegte Spannung eine negative Polarität bezüglich der Empfangsfläche besitzt. 40
9. Vorrichtung zum Schreiben auf einer Empfangsfläche mittels der Emission von Atomen aus einer Quelle der Atome, wobei die Quelle die Spitze eines abrasternden Fühlers aus Draht ist und die Vorrichtung Mittel zum Halten der Spitze innerhalb des Atomtransferbereichs der Empfangsfläche beinhaltet, dadurch gekennzeichnet, daß die Vorrichtung 45

außerdem Mittel zur abrasternden Führung der Fühlerspitze lateral über die Empfangsfläche hinweg und Mittel zum Anlegen einer Reihe von Spannungsimpulsen an den Draht beinhaltet, um die Emission von Atomen aus demselben zu bewirken, wobei das Material des Drahtes der Migration von Atomen unterworfen ist, um die Spitze unter dem Einfluß der Spannungsimpulse kontinuierlich neu zu bilden.

10. Verwendung einer Vorrichtung gemäß Anspruch 9 zum Lesen des durch das Verfahren irgendeines der Ansprüche 1 bis 8 erzeugten Geschriebenen, welche die Schritte der abrasternden Führung der Spitze über das Geschriebene auf der Empfangsfläche hinweg und die Erfassung einer Schwankung eines Tunnelstroms zwischen der Spitze und der Empfangsfläche beinhaltet. 50
11. Verwendung einer Vorrichtung gemäß Anspruch 9 zum Löschen des durch das Verfahren irgendeines der Ansprüche 1 bis 8 erzeugten Geschriebenen, wobei die Spitze innerhalb des Tunnelstrombereichs der aufgebrachten Atome positioniert und die Spitze Spannungsimpulsen mit einer Höhe und Polarität unterworfen wird, um die aufgebrachten Atome auf die Spitze zu ziehen. 55

Revendications

1. Procédé d'inscription sur une surface réceptrice par l'émission d'atomes provenant d'une source d'atomes, dans lequel la source est une sonde de balayage à fil comportant une pointe positionnée à une portée de transfert d'atomes de la surface réceptrice, caractérisé en ce que l'on fait balayer la pointe latéralement sur la surface réceptrice tout en la soumettant à une série d'impulsions de tension qui sont d'une amplitude et d'une durée telles qu'elles provoquent l'émission d'atomes depuis le fil jusque sur la surface réceptrice, et les impulsions de tension agissent pour amener la pointe de la sonde à se reformer continuellement par la migration des atomes de la sonde à fil vers la pointe. 30
2. Procédé selon la revendication 1 dans lequel la pointe est positionnée à la portée d'un courant par effet tunnel de la surface réceptrice. 35
3. Procédé selon la revendication 2 comprenant en outre l'étape consistant à détecter les variations du courant par effet tunnel entre la pointe et la surface réceptrice afin de commander le positionnement de la pointe. 40
4. Procédé selon la revendication 1, 2 ou 3, dans lequel le fil est fait d'un matériau sélectionné parmi 45

l'or, l'argent, le plomb, le cuivre l'indium, le cobalt, le nickel, le fer, le niobium, le platine, le titane ou l'aluminium.

5. Procédé selon l'une quelconque des revendications précédentes dans lequel le fil est chauffé. 5
6. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le fil est fait d'or et n'est pas chauffé. 10
7. Procédé selon l'une quelconque des revendications précédentes dans lequel la tension appliquée au fil dépasse 2 volts par nanomètre de distance séparant la pointe de la surface réceptrice. 15
8. Procédé selon l'une quelconque des revendications précédentes dans lequel la tension appliquée au fil présente une polarité négative par rapport à la surface réceptrice. 20
9. Appareil destiné à faire une inscription sur une surface réceptrice par l'émission d'atomes provenant d'une source d'atomes, dans lequel la source est la pointe d'une sonde à fil de balayage et l'appareil comprend un moyen destiné à maintenir la pointe à la portée du transfert d'atomes de la surface réceptrice, caractérisé en ce que l'appareil comprend également un moyen destiné à faire balayer la pointe de sonde latéralement sur la surface réceptrice et un moyen destiné à appliquer une série d'impulsions de tension au fil afin de provoquer l'émission d'atomes à partir de celui-ci, le matériau du fil étant soumis à la migration des atomes afin de reformer continuellement la pointe sous l'influence des impulsions de tension. 25
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10. Utilisation d'un appareil selon la revendication 9 afin de lire l'inscription formée par le procédé de l'une quelconque des revendications 1 à 8, comprenant les étapes consistant à faire balayer ladite pointe sur l'inscription qui est sur la surface réceptrice et à détecter les variations du courant par effet tunnel entre la pointe et la surface réceptrice. 40
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11. Utilisation d'un appareil selon la revendication 9 afin d'effacer l'inscription formée par le procédé de l'une quelconque des revendications 1 à 8, dans laquelle ladite pointe est positionnée à la portée du courant par effet tunnel des atomes déposés et la pointe est soumise à des impulsions de tension d'une amplitude et d'une polarité telles qu'elle attire sur la pointe les atomes déposés. 50

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